

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



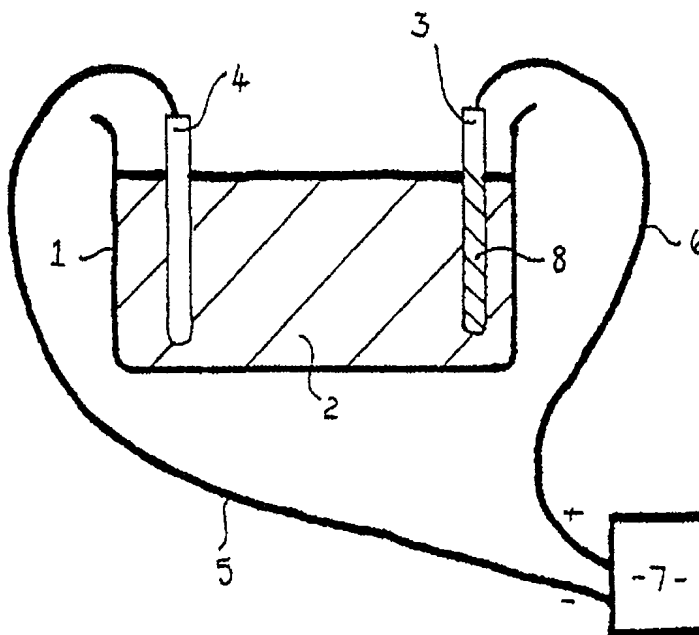
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C23C 22/84</b>		A1	(11) International Publication Number: <b>WO 98/42892</b>
			(43) International Publication Date: 1 October 1998 (01.10.98)
(21) International Application Number: PCT/NZ98/00040		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 23 March 1998 (23.03.98)			
(30) Priority Data: 314467 24 March 1997 (24.03.97) NZ 328316 11 July 1997 (11.07.97) NZ 328719 11 September 1997 (11.09.97) NZ			
(71) Applicant (for all designated States except US): MAGNESIUM TECHNOLOGY LIMITED [NZ/NZ]; 137 Captain Springs Road, Onehunga, Auckland (NZ).		Published With international search report.	
(72) Inventors; and (75) Inventors/Applicants (for US only): MacCULLOCH, John, Arnold [NZ/NZ]; 4/568 Remuera Road, Remuera, Auckland (NZ). ROSS, Phillip, Nicholas [NZ/NZ]; 31 Lowther Place, Taradale, Napier (NZ). HENSHAW, Geoffrey, Stephen [NZ/NZ]; 3/153 Victoria Avenue, Remuera, Auckland (NZ).			
(74) Agents: CALHOUN, Douglas, C. et al.; A.J. Park & Son, Huddart Parker Building, 6th floor, Post Office Square, P.O. Box 949, Wellington 6015 (NZ).			

(54) Title: ANODISING MAGNESIUM AND MAGNESIUM ALLOYS

(57) Abstract

This invention provides a method for the anodisation of magnesium or magnesium based alloys using an electrolytic solution (preferably derived primarily from phosphoric acid) containing ammonia, amines or both. The use of such an aqueous electrolytic solution (irrespective of other additions) in at least preferred forms alters the conditions under which anodisation can occur to provide a more than satisfactory coating on the magnesium material with reduced cycle times.



*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon			PT	Portugal		
CN	China	KR	Republic of Korea	RO	Romania		
CU	Cuba	KZ	Kazakhstan	RU	Russian Federation		
CZ	Czech Republic	LC	Saint Lucia	SD	Sudan		
DE	Germany	LI	Liechtenstein	SE	Sweden		
DK	Denmark	LK	Sri Lanka	SG	Singapore		
EE	Estonia	LR	Liberia				

## ANODISING MAGNESIUM AND MAGNESIUM ALLOYS

This invention is a method for the anodisation of magnesium and its alloys which, at least in the preferred form, produces an even and corrosion resistant film and which, at least in the preferred form, is suitable as a pre-treatment for other processes or as a final treatment for magnesium articles.

Magnesium is a very light, yet strong metal and is finding increasing acceptance for metal die castings, particularly where weight savings are desired. In addition, its property of shielding electromagnetic radiation is causing it to be of interest as a replacement for plastics in applications such as computers and mobile telephones. However, it is a reactive metal and corrosion, whether general or by galvanic effects, is a major problem.

Traditionally, a number of methods for applying a protective anodic oxide film on magnesium metal have been available. These have sought to imitate the well established processes available for coating aluminium and its alloys, but achieving the same result on magnesium articles has been extremely difficult. In part this is due to the fact that the oxide formed from a given volume of magnesium metal occupies less space than the original metal and thus any film of the oxide formed on the surface is subject to tensile stress and before a significant layer can be built up, it cracks and spalls away from the substrate.

The anodisation of aluminium and its alloys is often conducted in sulphuric acid in which the oxide layer formed is slightly soluble. As the film builds outwards from the metal substrate, its rate of build decreases, so ultimately there is a point at which the rate of dissolution is equal to that of further film growth. The dissolution of the film causes the formation of pores through which the ionic migration necessary to the electrochemical oxidation of the metal takes place. Without these pores only very thin films would be possible. After the electrochemical oxidation process is complete, the pores are sealed. Sealing of anodised aluminium can be achieved with hot water or simple inorganic chemical solutions.

Clearly an analogous process involving magnesium or alloys of magnesium would attempt to simulate these features. However, because of the tendency of the forming film to crack and break due to the imposed tensile stresses, there are complications. Also, the use of an acidic solution to anodise magnesium is fraught with serious difficulties as magnesium is rapidly attacked by most common acids. Therefore, we believe anodisation of magnesium should take place in alkaline solutions. Nevertheless some prior art processes use hydrofluoric acid or acid fluoride salts in which magnesium is not attacked because of the formation of a protective layer of magnesium fluoride on the metal surface.

This is not soluble in water and thus prevents further attack.

A further method of anodising magnesium or alloys of magnesium relies on this property to create a rough, very porous layer which forms an excellent base for paint or other surface coatings to be applied afterwards. Commonly, such an anodic film may be formed in an electrolyte of very high pH, containing alkali hydroxides. The process proceeds by means of sparking which sparking forms a sintered ceramic oxide film as the metal substrate is coated.

A number of proprietary methods for anodisation of magnesium or alloys of magnesium exist which seek to avoid this problem and create a uniform film. This can only be done by incorporating other species into the film as it is formed. Some processes use silicates. Others use various ceramic materials. Some of these processes involve the use of hydrofluoric acid or acid fluoride salts, eg; ammonium bifluoride. These are extremely hazardous materials causing fume and safety problems to the plant operators, and disposal problems.

In PCT/NZ96/00016 (WO 96/28591) (Barton) there is disclosed a viable procedure for anodising magnesium or magnesium alloys. It involves anodising the material in an ammonia containing electrolyte solution. The presence of some phosphate compounds in the solution is disclosed.

The object of the invention is to provide as an alternative to or as a refinement of the process of WO 96/28591 a process which also can produce an even film, or which at least provides the public with a useful choice.

## STATEMENTS OF INVENTION

In one aspect the present invention consists in **a method of anodising magnesium or magnesium alloys** comprising or including:

immersing said magnesium containing material in an electrolyte as an anode;  
providing a cathode in said electrolyte; and  
passing a current through said electrolyte;

**and wherein** the electrolyte, possessing a pH greater than 7, comprises or includes in water

(i) ammonia or an amine, or a mixture of the two, (preferably any ammonia being present in a concentration substantially in the range of 0.4 to 12 molar); and

(ii) phosphoric acid or a water soluble phosphate salt.

Preferably said phosphoric acid and said phosphoric acid is provided in the range of 0.05 to 0.2 molar.

Preferably said electrolyte contains a foaming agent.

Optionally said electrolyte contains a water soluble peroxide.

Preferably an amine is used alone for step (i) or as partial replacement for ammonia in step (i) and said amine is a water-soluble primary, secondary or tertiary amine having a pKa greater than 5.

5 Preferably said amine has a pKa greater than 9.

Preferably the magnesium or magnesium alloy article is cleaned by a pretreatment step prior to anodisation.

Preferably the pre-treatment step includes at least one of the following:

10 (A) immersion of the article in a mixture of sodium tetraborate and sodium pyrophosphate solution at 70°C to 90°C for approximately at least five minutes; or

(B) immersion of the article in 35% hydrofluoric acid (v/v) at ambient temperature for at least approximately one minute; or

15 (C) immersion of the article in a one to one mixture of 35% hydrofluoric acid (w/w) and 68% nitric acid (w/v) for at least approximately one minute.

Preferably the material is anodised using an electrical current having the following characteristics:

20 (I)(a) (i) a DC voltage (where the electrolyte includes ammonia and no amine) from 300 volts (and particularly 350 volts upwards) upwards; or  
(ii) a DC voltage (where the electrolyte includes an amine or ammonia and an amine) from 250 volts upwards; and

(b) *optionally*

25 (i) an AC voltage usually between zero to 40 volts, but under some circumstances more; and/or  
(ii) a pulsed (square wave form) voltage usually between zero and 40 volts, but sometimes greater; and

(II) a current density from 50 to 1000 amps per square metre.

Preferably the current density is from 200 to 350 amps per square metre.

30 In a further aspect the invention consists in a **method of anodising magnesium or a magnesium alloy** (hereafter "the magnesium material") comprising or including; providing an electrolytic solution;

providing a cathode in or for said solution;

placing the magnesium based material as an anode in said solution and,

35 passing a current between the anode and cathode through said solution so that an anodised surface results,

**and wherein the electrolyte**, possessing a pH greater than 7, comprises or includes in water

- (a) (i) ammonia and an amine or (ii) an amine  
and  
(b) (i) at least one source of phosphate ions, and/or (ii) at least one source of  
aluminate anions and at least one source of fluoride ions; **and wherein**  
5 the current applied during the anodisation is to a voltage limit  
(A) (i) if no hydrogen peroxide and/or a soluble peroxide is present in the  
electrolyte solution, greater than 220 Volts, and  
(ii) if hydrogen peroxide and/or a soluble peroxide is present in the  
electrolyte solution, greater than 210 Volts, and  
10 (B) below that which provides any substantial degree of spark formation on the  
magnesium material or its anodising surface as anode and/or plasma discharges yet is  
higher than would otherwise be possible without any substantial degree of spark formation  
on the magnesium material or its anodising surface and/or plasma discharges were it not  
for the ammonia and/or amine presence in the electrolyte solution.  
15 Preferably said amine is capable in alkaline solution of expressing ammonia gas  
or a volatile amine moiety.  
Preferably said electrolyte solution includes at least one source of phosphate ions.  
Preferably there is a source of phosphate ions and none of the optional aluminate  
and fluoride ions.  
20 Preferably the anodisation is carried out whilst the electrolyte solution is below  
50°C.  
Preferably the voltage limit is in the case of (A) (i) greater than 300 Volts and  
preferably less than 600 Volts, and in the case of (A) (ii) greater than 280 Volts and  
preferably less than 550 Volts.  
25 Preferably the aqueous electrolyte solution contains at least 3% w/v ammonia  
(when expressed as ammonia gas).  
Preferably the aqueous electrolyte solution contains 5% w/v ammonia or above  
(when expressed as ammonia gas).  
Preferably at least one source of phosphate ions is selected from the group of  
30 phosphoric acid, soluble phosphate salt(s) and soluble ammonium phosphate(s).  
Preferably the phosphate ions have been obtained by adding phosphoric acid to the  
bath thereby forming various phosphate anions by hydrolysis.  
Preferably a source of phosphate ions in the range of from 0.01 to 0.2 molar is  
present.  
35 Preferably the source of phosphate ions are present at about 0.05 to about 0.15  
molar.  
Optionally hydrogen peroxide or a soluble peroxide is present.

Optionally the electrolyte solution contains in addition at least one of the group of aluminates, silicates, borates, fluorides, phosphates, citrates and phenols.

Preferably the electrolyte solution is free of any substantial presence of chromium (III) and chromium (VI).

5 Preferably the electrolyte solution contains no alkali salt yielding hydroxide ions upon hydrolysis.

In still another aspect the invention consists in a **method of anodising magnesium based material** (ie; magnesium or magnesium alloys) comprising or including providing an electrolytic solution **and wherein the electrolyte**, possessing a pH greater than 7, comprises or includes in water

10 (a) (i) ammonia and an amine or (ii) an amine and  
(b) (i) at least one source of phosphate ions, and/or (ii) at least one source of aluminate anions and at least one source of fluoride ions;  
15 providing a cathode in or for said solution;  
placing magnesium based material as an anode in said solution; and  
passing a current between the anode and cathode through said solution so that an anodised surface is formed on said material,

**wherein**  
20 said ammonia and/or amine in said electrolytic solution is provided in sufficient quantity to avoid sparks and/or plasma-discharges during the anodisation process that cause partial melting or fusion of the anodised surface layer, and  
**wherein** said electrolyte solution comprises or includes water and a source of phosphate ions provided in the range of .01 to 0.2 molar, and

25 **wherein**  
said source of phosphate ions is selected from the group of phosphoric acid or a soluble phosphate salt (eg; a sodium hydrogen phosphate, ammonium sodium hydrogen phosphate, ammonium dihydrogen phosphate, and diammonium hydrogen phosphate).

Preferably said ammonia comprises at least 1% w/v of the electrolytic solution  
30 when expressed as a gas.

Preferably a magnesium or magnesium alloy article anodised by a method of any one of the preceding claims.

Preferably said magnesium containing article contains not less than 50% magnesium by weight.

35 In still a further aspect the invention consists in a method of anodising magnesium or magnesium alloys comprising or including operating an anodising system of an electrolyte solution, a cathode and the magnesium or magnesium alloy material as the or

an anode, wherein the electrolyte solution contains (i) an amine or amines or (ii) (a) an amine or amines and (b) ammonia in solution, in electrical input conditions which but for the inclusion of the amine(s) and any ammonia in the solution would not provide a coherent anodised coating (whether owing to so-called "sparking" or otherwise).

5 As used herein reference to ammonia presence as the gas by w/v% is after any neutralisation by any acid moieties.

Preferred embodiments of the invention will now be described with reference to the drawings in which Figure 1 shows a diagrammatic view of an anodisation bath in accordance with one embodiment of this invention.

10

### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The method for the anodisation of magnesium containing material (such as magnesium itself or its alloys) disclosed in WO 96/28591 has been further investigated by us. The process has been found to be useful on substantially pure magnesium samples as well as magnesium alloys such as AZ91 and AM60 which are common magnesium alloys used in casting.

15 The process of WO 96/28591 and also of this invention utilised a bath 1 having a solution 2 into which the magnesium containing material 3 may be at least partially immersed.

20 Electrodes 3 and 4 are provided in the bath 1 and into the solution 2, the solution 2 being an electrolytic solution.

Suitable connections such as cables 5 and 6 are provided from the electrodes 3 and 4 to a power supply 7.

25 The solution 2 is provided to include ammonia to a suitable concentration. The concentration of the ammonia in the electrolytic solution 2 may vary. However, a preferred range of between 1% and 33% w/v, ammonia (when expressed as the gas) is desirable.

30 As disclosed in WO 96/28591 it has been found that solutions in which the concentration of ammonia is below 1% w/v tend to cause some sparks to form with the method of formation of the coating tending more towards a coating formed through spark formation similar to prior art methods of anodisation. A 33% maximum concentration of ammonia acts as an upper limit.

We have found the ammonia concentration to work suitably in the region of 5 to 10% w/v or, more preferably, 5 to 7% w/v.

35 We have found it best when a current from the power supply 7 is passed through suitable connections (such as cables 5 and 6) to the electrodes 3 and 4 immersed within the electrolytic solution 2 when the voltage is in the approximate range of 220 to 250 V



DC. It should be noted that the prior art anodisation processes prior to the Barton process occur between 50 and 150 V DC and, therefore, a reduction of the concentration of ammonia below the desired level tends to allow sparks to form through the process taking up the properties of the prior art alkaline hydroxide anodisation processes before the voltage can reach a level suitable to form the coating in accordance with the present invention. Other embodiments can allow the process to operate within the approximate range of 170 to 350 V DC.

In a process such as this embodiment, the formation of sparks can occur for a number of reasons. The ammonia acts to repress sparks generally, but the concentration of salts in the bath also has an effect. If the ammonia gets too low, sparks may form. If the concentration of phosphate is increased greatly, sparks may occur at higher voltages, though the coating may form completely before the voltages are increased to such a voltage.

In a further embodiment, peroxide may be added to the electrolytic solution. The addition of peroxide has been observed to decrease the voltage at which the coating forms without spark formation. For example, a solution of 5% w/v ammonia (expressed as the gas), 0.05M sodium ammonium hydrogen phosphate and 0.1M sodium peroxide or hydrogen peroxide produces a coating at 210 V DC very similar to a 300 V DC coating formed in the absence of the peroxide. This may be advantageous in circumstances where a lower operating voltage is desired.

It has been further observed that decreasing the level of peroxide to 0.05M produces no significant difference to the coating than the example with no peroxide. Further, increasing the peroxide to 0.2M appears to prevent any reasonable coating being formed due to the presence of damaging sparks.

On this basis, a further preferred embodiment in which peroxide is added at, approximately, 0.1M may allow lower operating voltages if desired.

Upon application of the current to the electrolytic solution 2, a coating forms on the material 3 forming the anode on that portion 8 of the material 3 which is immersed within the solution 2. The process itself is, to a large degree, self terminating with the current drawn by the anodising bath 1 falling off as the depth of coating on the portion 8 increases. In this manner, the placement of an article 3 as an anode within the anodising bath 1 tends to draw current until the coating is formed and when sufficient coating exists to substantially isolate the magnesium in the material 3 from the electrolytic solution 2, the current drawn falls and can act as an indicator that the coating has been applied.

A number of additives may be provided in the solution 2 to alter the final coating and its appearance. For example, phosphate compounds may be used to provide a finish similar to anodised aluminium and it has been found that phosphate compounds provided

in the range of 0.01 to 0.2 molar can be suitable. Generally a concentration less than 0.01 molar tends to provide a finish which is somewhat transparent. Concentrations greater than 0.2 molar lead to an opaque finish which again alters the appearance of finished product. A preferred range of 0.05 to 0.15 molar of a phosphate compound such as ammonium sodium hydrogen phosphate has been found to be suitable if it is desired to provide a finish similar in appearance to anodised aluminium. The ammonium phosphate has been found particularly useful and other ammonium phosphate compounds could act as direct substitutes.

Anodisation using the ammonium phosphate compounds give significant corrosion resistance to the coating. Also the coating is particularly suited to further coating with paint or other organic sealers.

In further preferred forms of the invention, the electrolytic solution 2 may contain compounds such as ammonium dihydrogen phosphate, or alternatively or additionally, diammonium hydrogen phosphate. Both of these compounds may be more readily available in commercial quantities for the anodisation process compared with compounds such as ammonium sodium hydrogen phosphate.

An alternative additive to provide a finish similar to anodised aluminium has been found to be the use of fluoride and aluminate in similar concentrations to the phosphate compounds. Typical concentrations of compounds such as sodium aluminate and sodium fluoride are 0.05 molar of each of these compounds. As the concentration of sodium aluminate and sodium fluoride is increased towards 0.1 molar, the finish changes to a pearl coloured finish. Although this may be aesthetically pleasing in itself, it is not directly comparable with the anodised aluminium finish and, therefore, may be less suitable if it is desired to manufacture components for the same product from the different materials and be able to provide matching finishes on both aluminium and magnesium products.

The process itself is conducted at relatively low currents compared with the previous anodisation of magnesium processes. The current drawn is in the order of 100 amps per square metre of magnesium surface. The low current and lack of spark formation lead to a decrease in the temperature rise within the bath 1 to form an equivalent depth of coating compared with the alkaline hydroxide baths used previously. This reduction in the temperature rise of the bath leads to a significant decrease in the cooling equipment necessary to conduct the process.

Current preferred forms of the invention have been conducted at room temperature and it is preferred, although not essential, to conduct the anodisation process at less than 40°C.

It should be noted that the choice of additives includes a phosphate additive and/or

5 a fluoride additive. If the fluoride additive is used in substitution for the phosphate additive, this leads to greater problems with the disposal of the solution. Fluoride compounds are environmentally costly owing to stringent environmental regulation of their effluent and disposal. By comparison, the phosphate compounds are less damaging to the environment and may be preferred for this reason alone.

The additives may also include sealants or other compounds and many of the additives used in the previous anodisation processes such as aluminates, silicates, borates, fluorides, phosphates, citrates and phenol may be used.

10 The coating formed on the magnesium may be a mixed coating of magnesium oxide and magnesium hydroxide with further constituents according to any particular additives used in the process. For example, the embodiment in which sodium ammonium hydrogen phosphate is provided leads to a magnesium phosphate component in the coating. Further, the embodiment in which fluoride and aluminate compounds are provided may lead to the presence of magnesium fluoride and magnesium aluminate in  
15 the finished coating.

It should further be noted that the use of ammonia in the solution may necessitate the use of ventilation in the area about the anodisation bath 1.

The process as defined also tends to provide the coating somewhat faster than the prior use of alkaline hydroxide solutions.

20 A most preferred electrolyte composition where ammonia alone is used is:  
ammonia - 3.0-3.3 molar\* (usually made up from 25% aqueous solution);  
phosphoric acid - 0.1-0.2 molar (alternatively a phosphate salt may be used); and  
a foaming agent - 0.1ml per litre of a non-ionic foaming agent.

This bath has a pH of approximately 11.6.

25 \*The ammonia concentration is 3.0 to 3.3 molar after the addition of the phosphoric acid, hence the ammonia added initially to the bath is slightly more than this.

The foaming agent ideally has the effect of reducing ammonia loss to the atmosphere.

30 The most preferred electrochemical conditions for anodisation with such a composition comprise:

(I)(i) DC Voltage endpoint - 350V to 500V depending on desired film thickness;  
*and optionally:*

(ii)(a) AC Voltage set point - zero to 40V; *and/or*

(ii)(b) Pulsed Voltage set point - zero to 40V; and

35 (II) Bulk DC current density - 150-400 amps per square metre.

The temperature is in the range from 0°C to 35°C (most preferably 10-30°C).

The present invention recognises that partial or complete substitution of the ammonia

by an amine may be made whilst otherwise operating a process as disclosed in WO 96/28591 but under the conditions previously disclosed for the present invention.

Simple amines, such as methyl or ethyl amine are volatile so it is recommended that any substitution involve a longer chain or more complex amine. Suitable amines must be water soluble at least to a level of 3.0 molar and should feature basicity similar to that of ammonia (ability to form hydroxyl, OH<sup>-</sup> ions in solution). Some examples of amines that may be used are diethylene triamine and ethanolamine.

As mentioned above, a different anodising voltage may be used, and this will most preferably be from 250V DC upwards, with AC voltage imposed additionally as may be required.

The present invention in some preferred forms will now be described by reference to examples.

#### Example 1

An AZ91D magnesium plate was pre-cleaned in a solution containing 0.2 molar sodium tetraborate and 0.07 molar sodium pyrophosphate. This was then anodised in an electrolyte comprising 4.9% ammonia (expressed as w/v NH<sub>3</sub>) and 0.2 molar diammonium hydrogen phosphate at a voltage that peaked at 400V DC at a bulk current density of 200 amps per square metre. After attainment of 400V, which took just over seven minutes, the power supply was cut off and an anodic film of 9 microns was observed on the sample. Total cycle time was 7 minutes.

#### Example 2

An AM50 magnesium component was anodised at 100 amps per square metre, up to an endpoint voltage of 350V DC. The electrolyte composition was 3% ammonia (expressed as w/v ammonia gas) and 0.2 molar diammonium hydrogen phosphate. The component received a rinse prior to anodisation but no other pretreatment. Upon attainment of the endpoint voltage, the power was maintained to the sample and held at 350V DC for approximately ten minutes. Upon rinsing the sample was found to have an anodic film of approximately 17 microns. The cycle time was approximately 30 minutes.

#### Example 3

An AZ91D magnesium plate was anodised in an electrolyte comprising ammonia at 8% concentration (w/v as ammonia gas) and phosphoric acid at 0.1 molar. The sample was pre-cleaned in a bath comprising 0.2 molar sodium tetraborate and 0.07 molar sodium pyrophosphate at 60°C for five minutes, then it was activated in a bath comprising 35% hydrofluoric acid (v/v) for one minute prior to anodisation. The anodisation was

conducted at 200 amps per square metre, using a DC power supply that attained 465V which was then held for five minutes. A coating of 21.8 microns resulted. The anodising cycle required a total of 26 minutes.

5

#### Example 4

An AZ91D magnesium plate was anodised in an electrolyte comprising ammonia at 5.0% (expressed w/v as ammonia gas), 0.1 molar phosphoric acid and 0.03 molar hydrogen peroxide. The plate was pre-cleaned as per example #3 above and activated as per example #3 above. It was then anodised using a power supply comprising a DC voltage that reached 385V, and an AC voltage which reached 52V. The DC current density was 280 amps per square metre while the AC current density peaked at 90 amps per square metre. The DC endpoint voltage was held for five minutes, then the sample was post-treated for two minutes in a bath containing 1.0 molar sodium dihydrogen phosphate at 60°C. The sample was found to have an anodic coating of 19.7 microns. The anodising cycle required a total time of 15 minutes.

10

15

#### Example 5

An AZ91D test plate was pre-cleaned in a bath comprising 0.2 molar sodium tetraborate and 0.07 molar sodium pyrophosphate as in example #3 above. It was then anodised in an electrolyte comprising 2.5% ammonia (expressed as ammonia gas) and 0.5 molar diethylene triamine (DETA), together with phosphoric acid at 0.1 molar, at a DC voltage that attained 360V which was held for five minutes. The current density was 200 amps per square metre. The plate was found to have an anodic coating of 28.2 microns. The total cycle time was 21 minutes for the anodising process.

20

25

#### Example 6

An AZ91D test plate was pre-cleaned in the mixture described in example #3 (but not activated). It was then anodised in a solution comprising 19.8% monoethanolamine (w/v) and 0.2 molar sodium dihydrogen phosphate at a DC voltage that attained 350V which was held for five minutes. The current density was 200 amps per square metres. The sample was found to have an anodic coating of 20.2 microns. The total anodising cycle time was 16 minutes 30 seconds.

30

35

Note: in the above examples, process times quoted represent anodising times, not including pre-cleaning or activation where these are specified, nor any post-anodisation treatments.

**CLAIMS:**

1. A method of anodising magnesium or magnesium alloys comprising or including immersing said magnesium containing material in an electrolyte as an anode; providing a cathode in or for said electrolyte; and  
5 passing a current through said electrolyte;  
**and wherein** the electrolyte, possessing a pH greater than 7, comprises or includes in water
  - (i) ammonia or an amine, or a mixture of the two, and
  - (ii) phosphoric acid or a water soluble phosphate salt.
- 10 1. A method of claim 1 wherein ammonia is present in a concentration of from 0.4 to 12 molar.
2. A method of claim 1 or 2 wherein (ii) is provided as phosphoric acid and said phosphoric acid is provided in the range of 0.05 to 0.2 molar.
4. A method of any one of the preceding claims wherein said electrolyte contains a  
15 foaming agent.
5. A method of any one of the preceding claims wherein said electrolyte contains a water soluble peroxide.
6. A method of claim 1 wherein an amine is used alone for step (i) or together with ammonia in step (i) and said amine is a water-soluble primary, secondary or tertiary amine  
20 having a pKa greater than 5.
7. A method of any one of the preceding claims wherein said amine has a pKa greater than 9.
8. A method of any one of the preceding claims wherein the magnesium or magnesium alloy article is cleaned by a pretreatment step prior to anodisation.
- 25 9. A method of claim 8 wherein the pre-treatment step includes at least one of the following:
  - (A) immersion of the article in a mixture of sodium tetraborate and sodium pyrophosphate solution at 70°C to 90°C for approximately at least five minutes;  
or
  - 30 (B) immersion of the article in 35% hydrofluoric acid (v/v) at ambient temperature for at least approximately one minute; or
  - (C) immersion of the article in a one to one mixture of 35% hydrofluoric acid (w/w) and 68% nitric acid (w/v) for at least approximately one minute.
10. A method of any one of the preceding claims wherein the material is anodised using  
35 an electrical current having the following characteristics:
  - (I)(a) (i) a DC voltage (where the electrolyte includes ammonia and no amine) from 300 volts upwards; or

- (ii) a DC voltage (where the electrolyte includes an amine or ammonia and an amine) from 250 volts upwards; and

(b) *optionally*

- (i) an AC voltage usually between zero to 40 volts, but under some circumstances more; and/or
- (ii) a pulsed (square wave form) voltage usually between zero and 40 volts, but sometimes greater; and

- (II) a current density from 50 to 1000 amps per square metre.

11. A method of claim 10 wherein the current density is from 200 to 350 amps per square metre.

12. A method for the anodisation of magnesium or a magnesium alloy (hereafter "the magnesium material") comprising or including;

providing an electrolytic solution;

providing a cathode in or for said solution;

placing the magnesium based material as an anode in said solution and,

passing a current between the anode and cathode through said solution so that an anodised surface results,

**and wherein the electrolyte, possessing a pH greater than 7, comprises or includes in water**

- (a) (i) ammonia and an amine or (ii) an amine
- and

- (b) (i) at least one source of phosphate ions, and/or (ii) at least one source of aluminate anions and at least one source of fluoride ions;

**and wherein**

the current applied during the anodisation is to a voltage limit

- (A) (i) if no hydrogen peroxide and/or a soluble peroxide is present in the electrolyte solution, greater than 220 Volts, and
- (ii) if hydrogen peroxide and/or a soluble peroxide is present in the electrolyte solution, greater than 210 Volts, and

(B) below that which provides any substantial degree of spark formation on the magnesium material or its anodising surface as anode and/or plasma discharges yet is higher than would otherwise be possible without any substantial degree of spark formation on the magnesium material or its anodising surface and/or plasma discharges were it not for the ammonia and/or amine presence in the electrolyte solution.

13. A method of claim 12 wherein said amine is capable in alkaline solution of expressing ammonia gas or a volatile amine moiety.

14. A method of claim 12 or 13 wherein said electrolyte solution includes at least one

source of phosphate ions.

15. A method of claim 14 wherein there is a source of phosphate ions and none of the optional aluminate and fluoride ions.

16. A method of claim 12 wherein the anodisation is carried out whilst the electrolyte solution is below 50°C.

17. A method of claim 12 wherein the voltage limit is in the case of (A) (i) greater than 300 Volts and preferably less than 600 Volts, and in the case of (A) (ii) greater than 280 Volts and preferably less than 550 Volts.

18. A method of claim 12 wherein the aqueous electrolyte solution contains at least 3% w/v ammonia (when expressed as ammonia gas).

19. A method of claim 18 wherein the aqueous electrolyte solution contains 5% w/v ammonia or above (when expressed as ammonia gas).

20. A method of claim 14 wherein the at least one source of phosphate ions is selected from the group of phosphoric acid, soluble phosphate salt(s) and soluble ammonium phosphate(s).

21. A method of claim 14 wherein the phosphate ions have been obtained by adding phosphoric acid to the bath thereby forming various phosphate anions by hydrolysis.

22. A method of claim 14 wherein a source of phosphate ions in the range of from 0.01 to 0.2 molar is present.

23. A method of claim 14 wherein the source of phosphate ions are present at about 0.05 to about 0.15 molar.

24. A method of claim 12 wherein hydrogen peroxide or a soluble peroxide is present.

25. A method of claim 1 wherein the electrolyte solution contains in addition at least one of the group of aluminates, silicates, borates, fluorides, phosphates, citrates and phenols.

26. A method of claim 12 wherein the electrolyte solution is free of any substantial presence of chromium (III) and chromium (VI).

27. A method of claim 12 wherein the electrolyte solution contains no alkali salt yielding hydroxide ions upon hydrolysis.

28. A method for the anodisation of magnesium based material (ie; magnesium or magnesium alloys) comprising or including

providing an electrolytic solution possessing a pH greater than 7, which solution comprises or includes in water

(a) (i) ammonia and an amine or (ii) an amine  
and

(b) (i) at least one source of phosphate ions, and/or (ii) at least one source of aluminate anions and at least one source of fluoride ions;



providing a cathode in or for said solution;  
placing magnesium based material as an anode in said solution; and  
passing a current between the anode and cathode through said solution so that an  
anodised surface is formed on said material,

5        **and wherein**

said ammonia and/or amine in said electrolytic solution is provided in sufficient  
quantity to avoid sparks and/or plasma-discharges during the anodisation process  
that cause partial melting or fusion of the anodised surface layer, and

10        **wherein** said electrolyte solution comprises or includes water and a source of  
phosphate ions provided in the range of .01 to 0.2 molar, and

**wherein**

said source of phosphate ions is selected from the group of phosphoric acid or a  
soluble phosphate salt.

15        29. A method of claim 28 wherein said ammonia comprises at least 1% w/v of the  
electrolytic solution when expressed as a gas.

30. A method of anodising magnesium or magnesium alloys comprising or including  
operating an anodising system of an electrolyte solution, a cathode and the magnesium or  
magnesium alloy material as the or an anode wherein the electrolyte solution contains (i)  
an amine or amines or (ii) (a) an amine or amines and (b) ammonia in solution, in  
20        electrical input conditions which but for the inclusion of the amine(s) and any ammonia  
in the solution would not provide a coherent anodised coating.

31. A magnesium or magnesium alloy article anodised by a method of any one of the  
preceding claims.

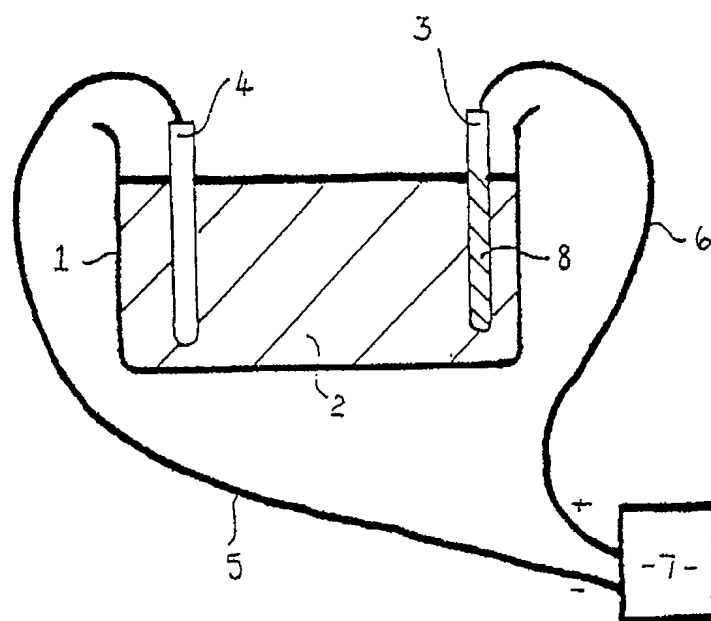
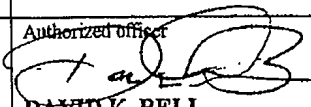


FIG. 1.

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/NZ 98/00040

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int Cl <sup>6</sup> : C23C 022/84		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) IPC6: C23C 022/84, C25D 011/30, 011/00, 011/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DERWENT: IPC6 AS ABOVE + MAGNESIUM + MG		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4978432 A (SCHMELING et al.) 18 December 1990 Whole document	1-2,6-11,28-31
X	WO 96/28591 A1 (INDUSTRIAL RESEARCH LTD) 19 September 1996 Whole document	1-31
A	US 4620904 A (KOZAK) 4 November 1986 Whole document	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search 22 May 1998		Date of mailing of the international search report -2 JUN 1998
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer  DAVID K. BELL Telephone No.: (02) 6283 2309

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NZ 98/00049

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5264113 A (BARTAK et al.) 23 November 1993 Whole document	
A	US 4551211 A (KOBAYASHI et al.) 5 November 1985 Whole document	

## INTERNATIONAL SEARCH REPORT

International Application No.

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

[illegible]